Electronic Supplementary Information

Novel Encapsulation of Water Soluble Inorganic or Organic Ingredients in Melamine Formaldehyde Microcapsules to Achieve Their Sustained Release in Aqueous Environment

Cong Sui,[ab] Jon A Preece,[c] Shu-Hong Yu[b] and Zhibing Zhang*[a]

[a] *School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom.*
E-mail address: Z.Zhang@bham.ac.uk

[b] *Division of Nanomaterials & Chemistry, Hefei National Laboratory for Physical Sciences at the Microscale, Collaborative Innovation of Suzhou Nano Science and Technology, Department of Chemistry, CAS Centre for Excellence in Nanoscience, Hefei Science Centre of CAS, University of Science and Technology of China, Hefei 230026, China.*

[c] *School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom.*

Experimental Section

Chemicals. Potassium chloride (KCl), allura red and formaldehyde (37% (aq.) w/w) were purchased from sigma-Aldrich, UK. MF precondensate (70 % wt (aq), formaldehyde to melamine molar ratio 0.2) was obtained from British Industrial Plastics Ltd, Birmingham, UK. Poly (acrylamide-acrylic acid, sodium salt) was bought from Polyersciences, Inc., US. Polyglycerol polyricinoleate (PGPR) was obtained from Palsgaard (Palsgaard 7130, Juelsminde, Denmark). Vegetable oil was bought from an Aldi store (Birmingham, UK), and hexane was ordered from Fisher Scientific, UK.

Synthesis of MF microcapsules with KCl/allura red encapsulated. KCl/allura red powder (0.1 g), MF precondensate (1.0 g), copolymer (0.232 g, poly(acrylamide-acrylic acid), sodium salt) and formaldehyde solution (200 µl/600 µl) were mixed in water (5 ml) homogeneously, and the aqueous solution was then adjusted by acetic acid to pH 4.3 (monitored by a pH meter) at room temperature. After the aqueous solution was mixed well, vegetable oil (400 ml) with polyglycerol polyricinoleate (0.8 g) was added immediately followed by stirring at 600 rpm for 2 h by a Rushton turbine (*Φ* 31 mm, in a vessel with standard configuration and full baffles) to form unripened MF microcapsules. The emulsion was heated to 55 ^{o}C, which was maintained for 30 min at the same stirring speed, and then stirred at 1200 rpm for another 30 min at the same temperature. After the temperature was adjusted to 75 ^{o}C for another 5 h heating, the ripened MF microcapsules were formed. Finally, NaOH solution (1 M, 2 ml) was dropwised (100 µl/min) by a syringe pump into the above vessel for 2 h at a stirring speed of 600 rpm to terminate the polymerisation process. The precipitate was centrifuged for 2 min at 6000 rpm (centrifugal force 4427 g), the supernatant decanted off, and the residue washed by hexane (35 ml x 3), and dried in a vacuum drier at room temperature for ~12 h, affording ~1 g of MF microcapsules. The MF-KCl microcapsules (ripened) formed with different volumes of formaldehyde solution (200 µl and 600 µl) were named as MF-KCl (200 F) and MF-KCl (600 F), respectively, and the MF-dye microcapsules (ripened) formed with formaldehyde solution (200 µl) were named as MF-dye (200 F).

Measurement of payloads, encapsulation efficiencies and release rates of KCl and

allura red. Payloads, encapsulation efficiencies and release rates of KCl and allura red were measured by a flame photometer (PFP-7, Jenway, UK) and a UV spectrophotometer at 504 nm (Cecil 2021 UV spectrophotometer), respectively. The MF microcapsules were ground using mortar and pestle to a fine powder, which were dissolved in aqua regia ($HCl : HNO_3 = 3:1$) overnight. The microcapsule debris was separated via centrifugation, and the supernatant solution was diluted with deionised water by a factor of 20. The concentration of K^+ in the solution was detected by the flame photometer. The payloads and encapsulation efficiencies of KCl and dye were calculated by Equations (S1) and (S2), respectively as follows:

$$\text{Payload} = \frac{\begin{array}{c}\text{Mass of KCl/dye recovered from}\\ \text{the obtained MF microcapsules}\end{array}}{\text{Mass of MF microcapsules}} \tag{S1}$$

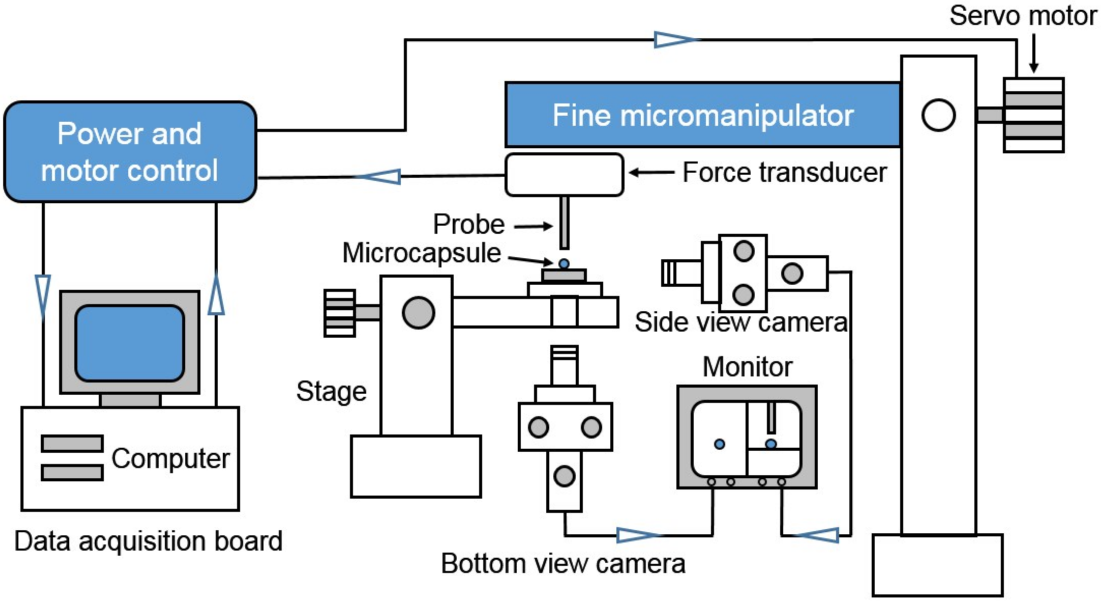
$$\text{Encapsulation efficiency} = \frac{\begin{array}{c}\text{Mass of KCl/dye recovered from}\\ \text{the obtained MF microcapsules}\end{array}}{\text{Mass of KCl/dye input}} \tag{S2}$$

The releases of KCl and allura red from the microcapsules were performed in deionised water (100 ml) in a Gallenkamp orbital shaker with a 150 rpm rotation speed at 37 ^{o}C. The released KCl/allura red samples (5 ml) were obtained periodically at fixed time intervals between 5 min to 12 h/10 days, and replaced by fresh deionised water (5 ml). The concentration of K^+ was measured by the flame photometer, and the concentration of allura red was detected by a UV spectrophotometer at 504 nm (Cecil 2021 UV spectrophotometer).

Sampling by ultra-microtome. A small amount of MF microcapsules was mixed with epon/araldite resin, which was polymerised at 60 ^{o}C overnight. A small trapezium shaped area was trimmed with a razor blade (approx. 0.3 mm x 0.3 mm). The face of the block was cut in an ultra-microtome (Reichert-Jung) using a glass knife. The block was coated with Pt and mounted on an SEM stub.

Micromanipulation. The mechanical properties of different batches of MF microcapsules were measured by a micromanipulation technique as shown in Scheme

S1. The sample dispersed in water was dried on a glass slide and mounted onto the stage, under a flat ending glass probe, which was connected to a force transducer (Model 402A, Aurora Scientific Inc., Canada). The transducer driven by a servo motor (Parker Compumotor, USA) could control the vertical compression movement. The voltage output was generated by the transducer, recorded by means of a data acquisition board in a computer, when a single microcapsule was compressed by the glass probe at a travelling speed of 2 μm/s. The whole compressing process was monitored through side and bottom view cameras and further displayed on the monitor screen. The voltage was hence converted to force, and the force versus displacement data of the microcapsules was obtained. Details of the micromanipulation device was described in the previous publication.[1]



Scheme S1. Illustration of the micromanipulation rig.

Other Characterisations. The viscosity of liquid was measured using a rheometer at a temperature of 15 (± 1) °C (AR1000, TA instruments, UK). The morphologies and cross-sections of the prepared microcapsules were observed with an optical microscope (301-371.011, Leica, Germany) and a Scanning Electron Microscope (SEM) (Philips XL-30 FEG ESEM). The cross-sections of the microcapsules were cut by a microtome (Reichert-Jung). The size distribution, SPAN and the mean volumetric size ($D_{4,\ 3}$) of the microcapsules were measured by a laser light scattering technique

(Mastersizer 2000, Malvern Instruments, UK). The FT-IR spectra were obtained using a Thermo Electron Nicolet 8700 spectrometer. The chemical composition of the sample was evaluated by an energy disperse X-ray microanalysis (EDX) (Oxford, Inca 300) in conjunction with SEM. The concentrations of KCl and allura red were measured by a flame photometer (PFP-7, Jenway, UK) and a UV spectrophotometer at 504 nm (Cecil 2021 UV spectrophotometer), respectively. The mechanical properties of microcapsules were determined by a micromanipulation technique.

All of the values are presented in mean value ± standard error of the mean except the viscosity, for which the figure after ± was estimated based on the maximum relative error (4%) specified in the instrument manual since the standard error from the repeated experiments is much smaller.

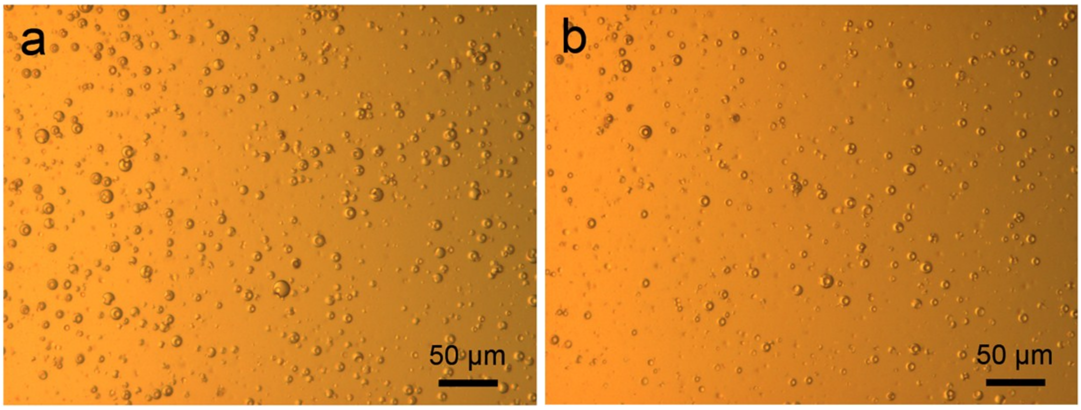


Figure S1. Optical micrographs of unripened MF-KCl (200 F) microcapsules generated (a) at 600 rpm, 55 ^{o}C for 30 min and (b) at 1200 rpm, 55 ^{o}C for 30 min after (a).

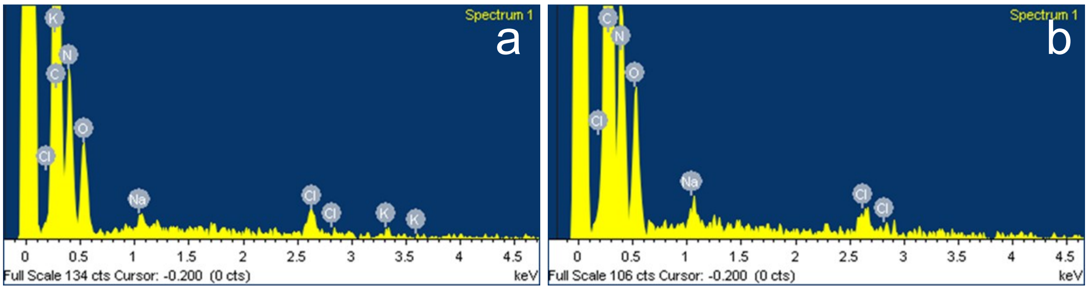


Figure S2. EDX analysis of (a) the core and (b) the shell of MF-KCl (200 F) microcapsule.

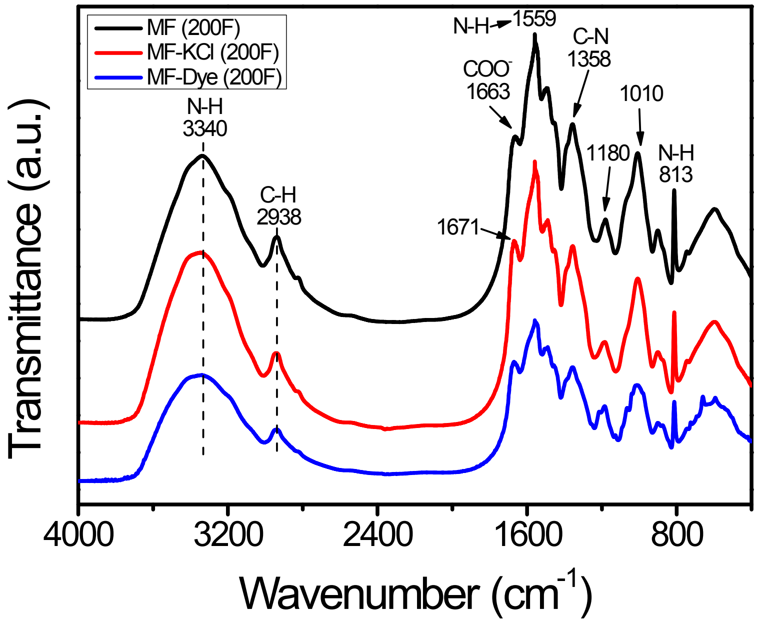


Figure S3. FT-IR spectra of MF (200 F), MF-KCl (200 F) and MF-dye (200 F) microcapsules.

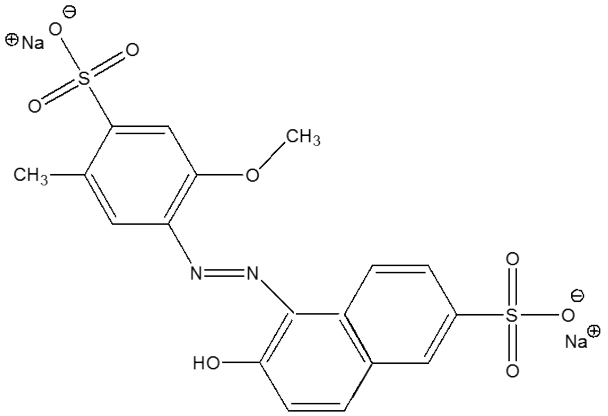


Figure S4. The chemical structure of allura red molecule.

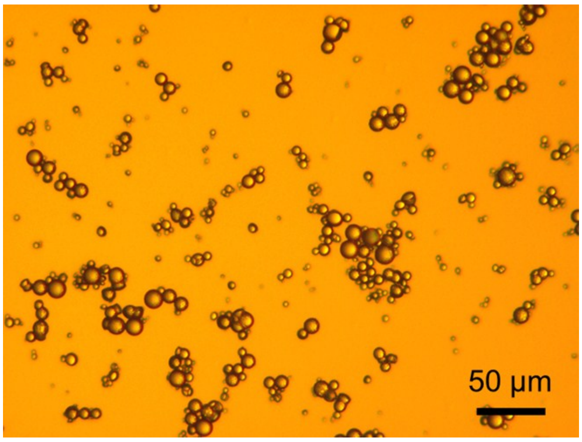


Figure S5. Optical micrograph of MF-KCl (200 F) microcapsules dispersed in ethanol for 2 month.

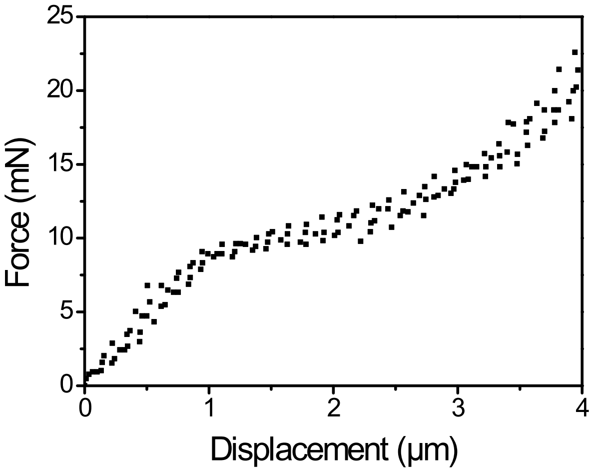


Figure S6. Typical force vs. displacement curve for compressing a single MF-KCl (200 F) microcapsule (diameter 9.7 μm).

Reference

1. Z. Zhang, R. Saunders and C. R. Thomas, *J Microencapsul*, 1999, **16**, 117-124.